Supporting Information for

A robust and scalable continuous process for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate

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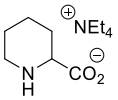
Preparation of catalysts

General procedure for the synthesis of homogeneous catalysts

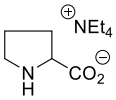
Catalysts were synthesized via simple acid-base neutralization reactions. A slight excess of carboxylic acid (1.1 equiv.) was added to an aqueous solution of tetraethyl ammonium hydroxide. The mixture was then stirred at room temperature for 2 h. After evaporation of water at 60 °C under reduced pressure, the residue was washed with methanol. Excess methanol was removed *in vacuo* after filtration and the residue was dried overnight on a high vacuum line.

Tetraethylammonium piperidine-2-carboxylate



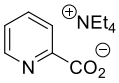
The title compound was prepared using the general procedure and all analytical data were found to be in accordance with the literature.[1]

Tetraethylammonium prolinate



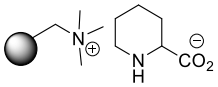
The title compound was prepared using the general procedure and all analytical data were found to be in accordance with the literature.[1]

Tetraethylammonium picolinate



The title compound was prepared using the general procedure and obtained as a yellow solid. ^{1}H-NMR (300MHz, D_2O, ppm): δ 8.55 (d, *J* = 3.5 Hz, 1H), 7.96 (td, *J* = 7.7, 1.6 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.50 (m, 1H), 3.23 (q, *J* = 7.3 Hz, 7H), 1.28 – 1.19 (m, 11H).

Polymer supported piperidine-2-carboxylate



Ambersep® 900 Hydroxide form resin (2 g, available from Sigma Aldrich) was added to an RBF containing pipecolic acid (1.3 g, 1.1 equiv.) in methanol (20 mL). The flask was shaken overnight at room temperature (orbital shaker). The polymer beads were filtered, washed with methanol and dried overnight under vacuum.

Calculation of relative flow rate for heterogeneous continuous column experiments

When using 3.5 equivalents of DMC, the following ratio should be achieved when mixing:

$$\frac{3.5\ mol\ DMC}{1\ mol\ glycerol} = \frac{315\ g\ DMC}{92\ g\ glycerol} = \frac{294\ mL\ DMC}{73\ mL\ glycerol} = 4.03$$

Note that this result is the required volume ratio when using both *neat* DMC and *neat* glycerol. This result changes when a solution of glycerol (5M) in methanol is used.

Therefore, the volume percent of glycerol is:

$$5\ M = \frac{5\ mol\ glycerol}{L} = \frac{460\ g\ glycerol}{1\ L} = \frac{365\ mL\ glycerol}{1\ L} = 0.365$$

Hence the relative flow rate becomes:

$$4.03 * 0.365 = 1.47$$

The relative flow rate of neat DMC should be about 1.47 times the flow rate of glycerol (5 M) in MeOH when 3.5 equivalents DMC are desired.

Calculation and assumptions for Space Time Yield calculations (STY)

The column reactors used in the construction of the flow reactor are Omnifit (10 mm i.d. x 100 mm). This would equate to a theroretical maximum internal volume of 7.85 mL per reactor. For a reaction of 5 M glycerol in MeOH at a flow rate of 2 mL/min (120 mL/h) using two columns and an isolated yield of 75% the STY would be calculated as follows:

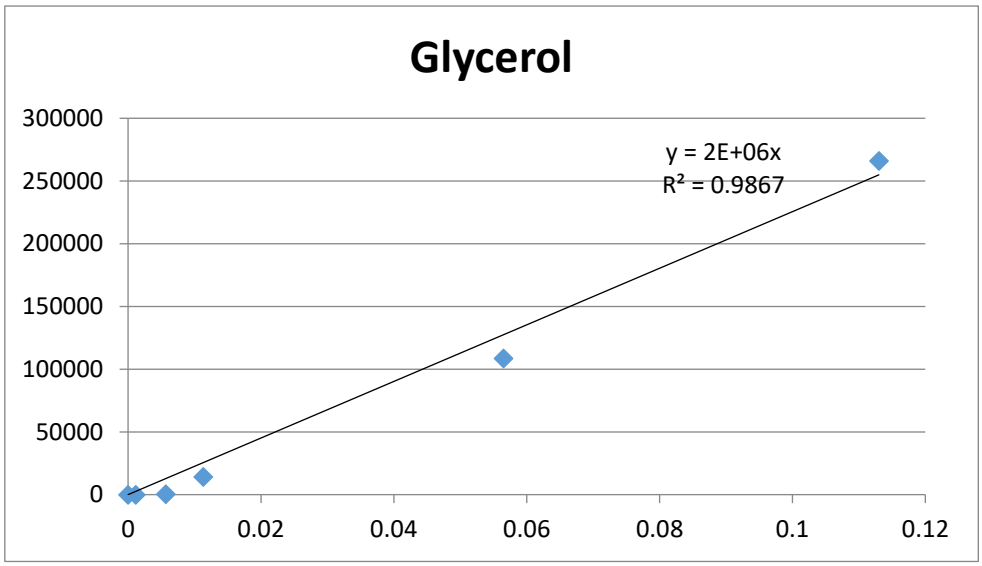
$$Throughput\ g/h = \ 120\ (Rt)\ \text{X}\ 118.09\ (\text{Mw})\ \text{X}\ \frac{5(M)}{1000}\text{X}\ 0.75\ = 53.1$$

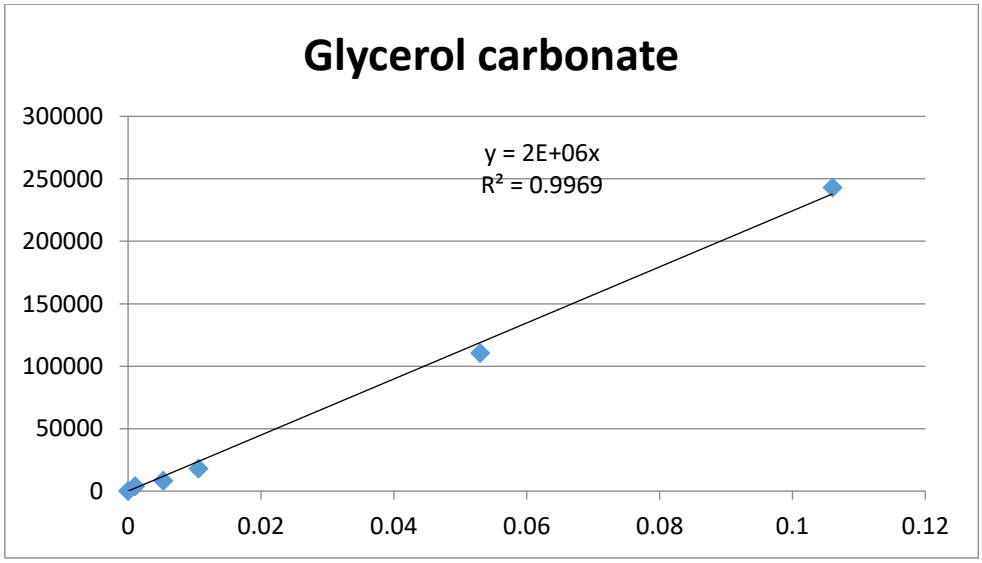
$$STY = \frac{1000\ (L)}{15.7\ (Rv)}\ \text{X}\ \frac{53.1}{1000} = 3.38\ kg\ per\ L\ per\ h$$

Rt = residence time, Mw = molecular weight of the product, Rv = reactor volume.

Calibration curves for glycerol and glycerol carbonate

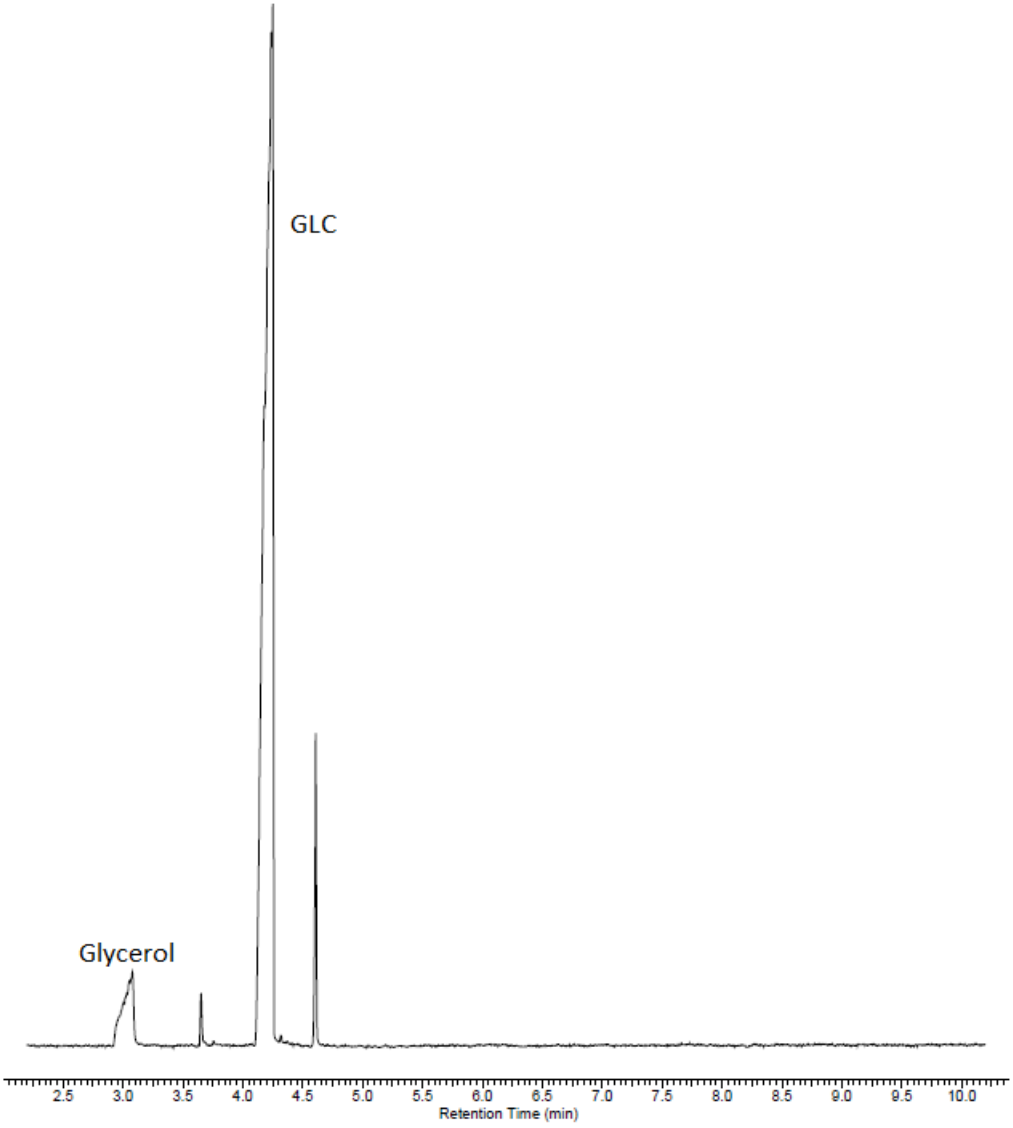
Several samples were prepared for following GC-MS experiment. Glycerol was dissolved in MeOH (0.113 M) and serial diluted to have samples in between 0.1 M and 0.001 M, the typical concentration range for prepared GC-MS samples. In the same way glycerol carbonate samples were prepared. The same response curve for peak area in function of concentration was obtained for both glycerol and glycerol carbonate. This was considered sufficient for estimation of GC yield, conversion and selectivity.



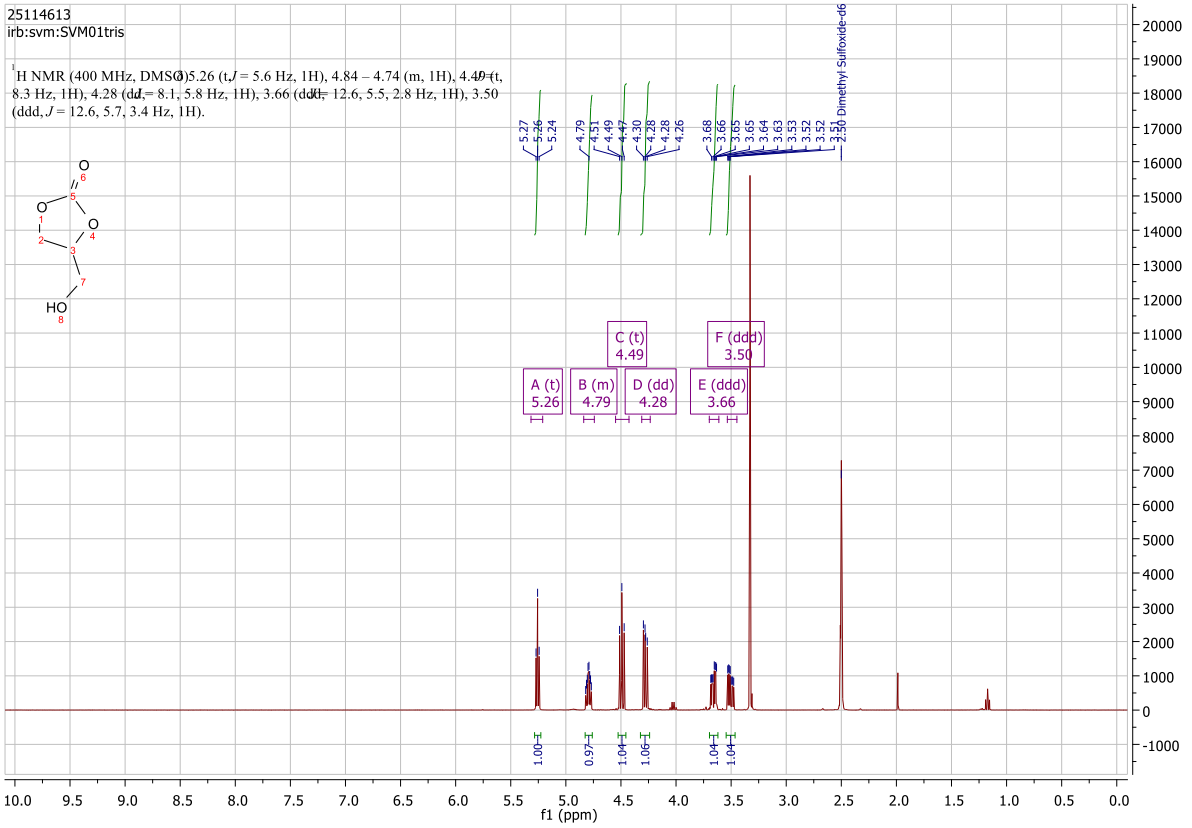


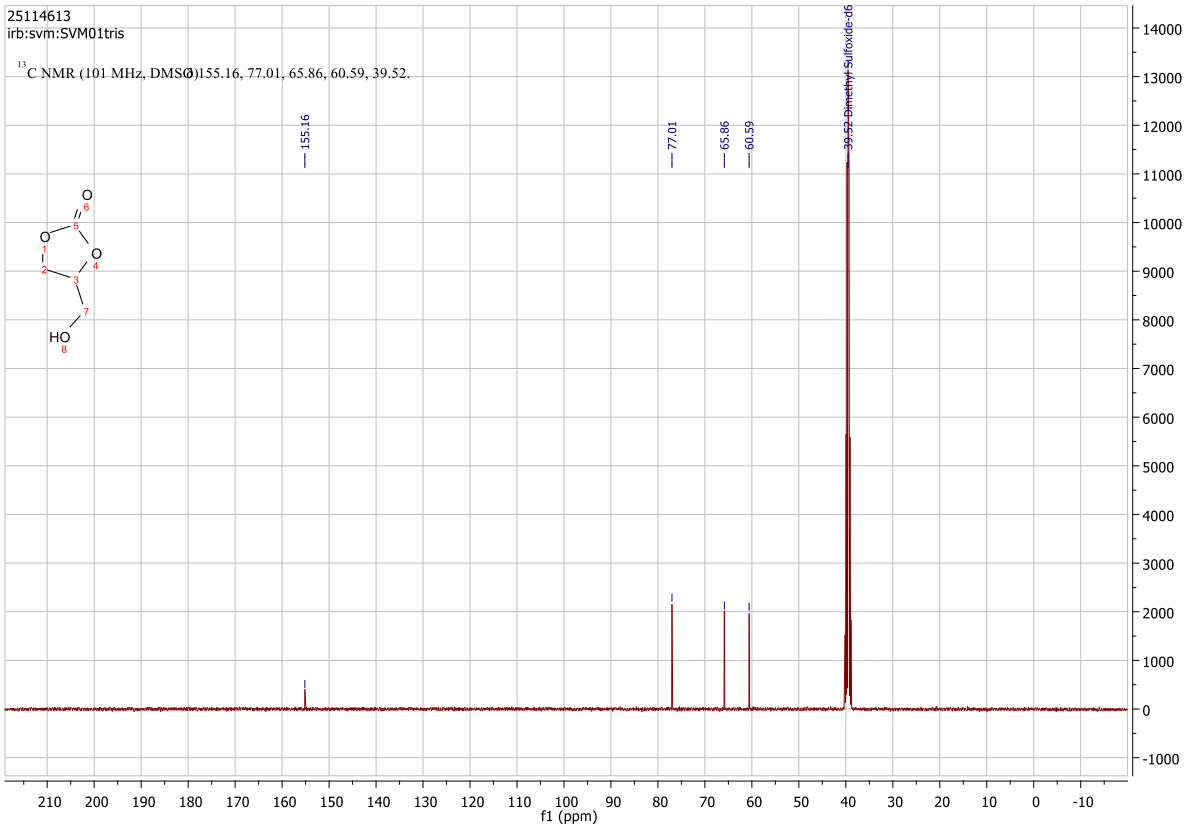
Standard GC Chromatogram

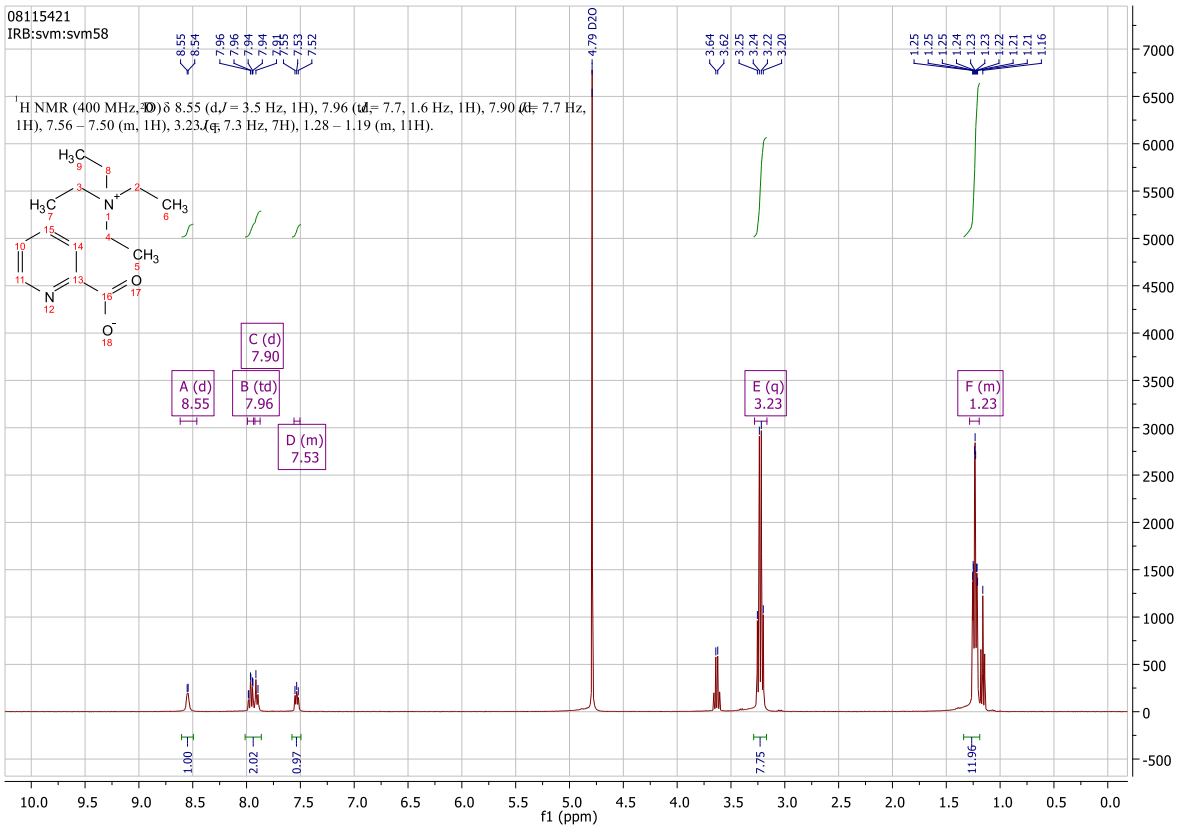
Comment	RemoteAnalyzer
Data Type	Centroided Mass Spectrum
Date	06 Jan 2016 13:19:57
Inlet Model	Other Probe
Ion Mode	CI-
Number of Scans	2400
Operator	Admin
Time Range	2.200-10.197



NMR spectra


25114613
irb:svm:SVM01tris
^{1}H NMR (400 MHz, DMSO) 5.26 (t, J = 5.6 Hz, 1H), 4.84 – 4.74 (m, 1H), 4.49 (t, 8.3 Hz, 1H), 4.28 (dd, J = 8.1, 5.8 Hz, 1H), 3.66 (ddd, J = 12.6, 5.5, 2.8 Hz, 1H), 3.50 (ddd, J = 12.6, 5.7, 3.4 Hz, 1H).
A (t) 5.26
B (m) 4.79
C (t) 4.49
D (dd) 4.28
E (ddd) 3.66
F (ddd) 3.50
2.50 Dimethyl Sulfoxide-d6
f1 (ppm)


25114613
irb:svm:SVM01tris
^{13}C NMR (101 MHz, DMSO) 155.16, 77.01, 65.86, 60.59, 39.52.
155.16
77.01
65.86
60.59
39.52 Dimethyl Sulfoxide-d6
f1 (ppm)



References

[1] Y. Zhou, F. Ouyang, Z. B. Song, Z. Yang and D. J. Tao, *Catalysis Communications* **2015,** *66*, 25-29.